

Influence of the dispersion medium on the properties of CdTe micro- and nanocrystals in a colloidal solution

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Surface and optical properties of CdTe nanoparticles obtained by grinding (40–150 nm, microcrystals) and colloidal synthesis (1–4 nm, nanocrystals) methods are investigated. It is shown that the most intensive adsorption of stabilizer molecules on the CdTe surface occurs when solvents are better wetting the surface of CdTe particles. It is found that the best stabilization of both the micro- and nanocrystals of CdTe is provided by using methyl and ethyl alcohol as the dispersion medium. The basic characteristics of photoluminescence of CdTe nanocrystals stabilized with thioglycolic acid in deionized water, methanol and ethanol of various concentrations are reported.

Keywords: cadmium telluride, nanocrystals, microcrystals, dispersion medium, photoluminescence.

Исследованы поверхностные и оптические свойства низкоразмерных структур на основе CdTe, полученного методами размолла (40–150 нм, микрокристаллы) и коллоидного синтеза (1–4 нм, нанокристаллы). Показано, что наиболее интенсивно адсорбция стабилизаторов на поверхности МК CdTe происходит из растворителей, которые лучше смачивают поверхность частиц телурида кадмия. Установлено, что стабилизацию частиц на основе CdTe в высокодисперсных и наноразмерных системах лучше всего проводить при использовании метилового и этилового спиртов в качестве дисперсионной среды. Приведены основные фотолюминесцентные характеристики стабилизированных тиогликолевой кислотой нанокристаллов CdTe, полученных при использовании в качестве дисперсионной среды деионизированной воды, метилового и этилового спиртов различной концентрации.

Вплив природи дисперсійного середовища на властивості мікро- та нанокристалів CdTe у колоїдних розчинах. *О.А.Капуш, С.І.Будзуляк, Д.В.Корбутяк, Н.Д.Вахняк, С.Д.Борук, В.М.Джаган, А.І.Ємець, М.Я.Валах.*

Досліджено поверхневі та оптичні властивості низькорозмірних структур на основі CdTe, отриманого методами розмолу (40–150 нм, мікрокристали) та колоїдного синтезу (1–4 нм, нанокристали). Показано, що найбільш інтенсивно адсорбція стабілізаторів на поверхні МК CdTe відбувається з розчинників, які краще змочують поверхню частинок кадмій телуриду. Встановлено, що стабілізацію частинок на основі CdTe в високодисперсних і нанорозмірних системах краще всього проводити при використанні метило-

вого і етилового спиртів в якості дисперсійного середовища. Наведено основні фотолюмінесцентні характеристики стабілізованих тіогліколевою кислотою нанокристалів CdTe, отриманих при використанні як дисперсійного середовища деіонізованої води, метилового та етилового спиртів різної концентрації.

1. Introduction

Semiconductor nanocrystals (NCs) or quantum dots (QDs) is an ever growing area of intense interdisciplinary research. Quantum confinement of electronic excitations in NCs results in new physical effects and the size-tunable properties give rise to a large number of prospective applications, such as solar energy conversion, light emitting diodes (LEDs), biolabeling, and photocatalysis [1–5]. The synthesis of nanoscale structures of a given size and the degree of dispersion is a challenging task that has become a subject of numerous studies. Among those, various methods of producing semiconductor nanocrystals have been proposed [6–10]. The main drawback of majority of the approaches is the complexity of controlling the NC size, leading to an unavoidable NC size spread distribution. The methods of aqueous synthesis of colloidal NCs or quantum dots of cadmium chalcogenides, attracted much attention, as most of them are relatively simple and safe [11–18]. CdTe NCs can possess as bright and sharp excitonic photoluminescence (PL) as NCs of other metal chalcogenides without the defect state emission that is common for other compounds [11, 19]. Colloidal synthesis allows the size and surface properties of NCs to be controlled, with best size spread distribution obtained being as low as ~ 5 % [11]. However NC properties obtained by colloidal synthesis depends on many process parameters (temperature, nature of the dispersion medium and stabilizer, the concentration of initial components and their ratio, pH etc.) [14, 20–27]. Moreover, most of the reports on colloidal synthesis of semiconductor NCs, particularly CdTe, are a largely consisting in checking a large range of synthesis parameters and their combination in order to obtain the NCs with optimized properties, e.g. maximum PL quantum yield at minimum size dispersion. The physical, or even chemical, mechanisms underlying in the formation of a certain NC ensemble are in many cases not investigated in details. However, these mechanisms are very important not only from the fundamental point of view but also from the point of view of future behavior of these NCs as a part of complicated nanodevices [28–33].

The aim of this work was to study the influence of commonly used dispersion media on the formation of micro- and nanocrystals CdTe stabilized by thioglycolic acid (TGA).

2. Experimental

CdTe microcrystals (MCs) were obtained by grinding single crystals grown by Bridgman. The 40–150 nm fraction was selected for investigation. To stabilize the surface of the obtained grinded CdTe MCs the TGA was used. As the dispersion medium a deionized water, methanol or ethanol were used. All chemicals used were of analytical grade or of the highest purity available.

The work of adhesion in the system CdTe/dispersion medium was determined by standard method [34, 35] by determining the geometrical dimensions of the dispersion medium droplets deposited on the surface of the crystal. In our case, the latter was the parental CdTe monocrystal from which the micro-particles were obtained by grinding. TGA adsorption on the surface of CdTe is dependent on the concentration of the stabilizer in solution before and after contact with an adsorbent (CdTe MCs). Stabilizer concentration was determined by the change of the refractive index of the solution using the interferometer LYR-2.

Colloidal CdTe nanocrystals (NCs) were obtained by low temperature colloidal synthesis in the reactor of complete mixing in the presence of TGA as a stabilizer. As the dispersion medium deionized water and aqueous solutions of methyl and ethyl alcohols were used. The concentrations of starting materials and other synthesis conditions are given in the Table 1.

Optical properties of obtained CdTe NCs were performed by PL spectroscopy. PL spectra were excited with 325.0 nm line of He–Cd laser (10 mW) and recorded using automated spectrometer MDR-23 equipped with uncooled photomultiplier FEU-100.

3. Results and discussion

As a first step of investigation surface and optical properties of CdTe micro- and nanocrystals obtained by two fundamentally different methods providing complementary NC size range were studied. 40–150 nm MCs obtained by grinding bulk single crys-

Table 1. Concentrations of precursors and conditions for the synthesis of NCs CdTe/TGA

Sample number	Concentration of reagents					pH	Synthesis duration, min
	CdI ₂ , mol	H ₂ Te, mol	TGA, mol	(CH ₃ OH), %	(C ₂ H ₅ OH), %		
I	2·10 ⁻³	2.49·10 ⁻⁴	5.7·10 ⁻³	0	0	10	2
II				1	0		
				2			
				3			
III	1	5					
	2	10					
	3	25					

tals (top-down approach) and 1–4 nm NCs obtained by colloidal synthesis (bottom-up approach).

Many properties of both micro- and nanocrystalline semiconductor are largely determined by the physical-chemical parameters of particle surface. Thus, controlling these properties, including resistance to aggregation and sedimentation, becomes possible only when a layer of proper stabilizers is formed on the surface. Adsorption of stabilizers typically reduces the size of the surface energy of particles of cadmium telluride, which contributes to the destruction of aggregates in dispersed systems, and prevents coagulation during sedimentation [36, 37]. The adsorption intensity, as well as the nature of the interaction between adsorbate (stabilizer) and CdTe surface are determined by both the properties of the CdTe surface and the physical and chemical nature of the molecules of stabilizer and dispersion medium. Formation of the adsorbed stabilizer layer occurs in a competition with adsorption of the solvent molecules. For understanding the structure of the adsorbed layer, both the type of distribution and filling sequence of the stabilizer molecules on semiconductor surface are important. In theory, three possible variants of the distribution of stabilizer molecules on the CdTe surface can occur. In case of a regular distribution, each successive molecule is adsorbed at the maximum possible distance from already adsorbed molecules. In case of statistical distribution a random attachment of the molecules takes place. Finally, when already bound to the surface molecules create favorable conditions for attachment of new molecules, an island-like distribution takes place [38, 39].

Fig. 1 shows the adsorption isotherm of TGA on the surface of CdTe MCs dispersed in water, methanol and ethanol. In all cases,

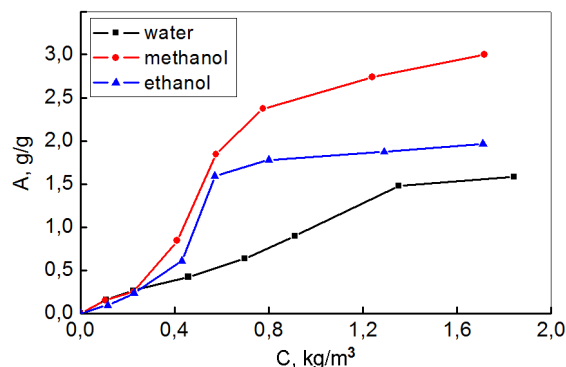


Fig. 1. Adsorption isotherms of TGA on CdTe MC surface in water, methanol, and ethanol.

the adsorption isotherm starts at origin of coordinates and is S-shaped.

It is seen that in the range of low concentrations of TGA (0.2–0.3 kg/m³) adsorption processes is characterized by low intensity for all three dispersion media (0.0025–0.0003 g/d) and occurs due to absorption of individual molecules of TGA.

With further increase in TGA concentration, a steep increase in the adsorption intensity begins. It is presumably due to the formation of molecular associates of TGA molecules (dimers, trimers) in the solution; adsorption of these associates leads to the formation of a thicker adsorption layer on the surface of CdTe, as illustrated schematically in Fig. 2. The latter adsorption is reversible, as confirmed by the experiments with TGA desorption.

The data obtained allows the following sequence of the TGA adsorption capacity on the surface of CdTe MCs to be deduced:

$$A(\text{methanol}) > A(\text{ethanol}) > A(\text{water}).$$

The observed trend to decrease of the adsorption capacity of TGA is presumably due to the intermolecular interactions in solution. The adsorption capacity reached maximum values in case of adsorption taking place in methyl and ethyl alcohol, which pos-

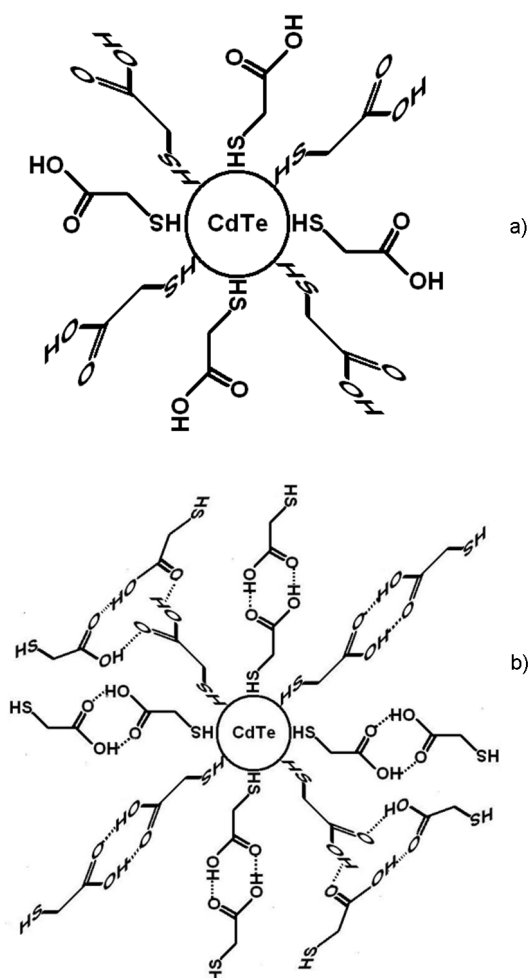


Fig. 2. Scheme of adsorption of TGA monomers (a) and associates (b) on the surface of CdTe MCs.

sess a good wettability of CdTe surface. The latter effect, in turn, is associated with low surface tension of these solvents ($\sigma_{\text{methanol}} = 22.61 \text{ mJ/m}^2$, $\sigma_{\text{ethanol}} = 22.03 \text{ mJ/m}^2$) and low values of the work of adhesion.

It should also be noted that the limit value of adsorption depends on the energy of adhesive interactions in the system dispersion medium — adsorbent (CdTe). The

analysis of the impact of the structure of the molecule of the dispersion medium on the energy of adhesive interactions in the system dispersion medium — crystalline CdTe showed that the maximum values of the work of adhesion is characterized for water-CdTe. This result was observed for the samples CdTe directly after the process of etching the crystal surface, as well as after storage in air for four weeks, $A = 103.56$ and 131.98 mJ/m^2 , respectively. It should be noted that the energy of adhesive interaction in the system water-CdTe varies notably with the storage time, but it is always higher for freshly etched samples compared with those after prolonged storage. The reason for that, in our opinion, is a gradual oxidation of the surface of cadmium telluride. Inclusion in the structure of the surface layer of oxygen atoms leads to the formation of additional hydrogen bonds and to increasing the interaction energy between the dispersion medium (water) and the solid state (CdTe) surface (Table 2).

In the systems methanol-CdTe and ethanol-CdTe the discussed above adhesive interactions are significantly reduced compared to water dispersion. The results obtained demonstrate (Table 2), that the former two solvents are characterized by minimal values of the work of adhesion. Furthermore, we have established that for the methanol- and ethanol-based systems, the work of adhesion does not depend on the time that has passed after etching the surface. Presumably, the area of the hydrophobic regions of the CdTe surface during oxidation is not significantly reduced, and the inclusion of new oxygen atoms in the structure of the surface layer does not affect the energy of adhesive interaction between the dispersion medium and the CdTe surface.

It should be noted that the interaction of the investigated solvents with the CdTe surface is limited to the dispersion interaction, as confirmed by experiments on the heat of

Table 2. The work of adhesion of the system "dispersion medium — crystalline CdTe"

Dispersion medium	State of the surface	Surface tension of the dispersion medium, mJ/m^2	Work of adhesion, mJ/m^2	$\cos \Theta$
Water	polished	72.75	131.98	0.814
	etched		103.56	0.424
Methanol	polished	22.61	44.67	0.976
	etched		44.77	0.980
Ethanol	polished	22.03	43.52	0.976
	etched		42.96	0.950

wetting of the surface of cadmium telluride. In all cases, upon introducing of the fine-grained (superfine) CdTe, preliminary dried at 353 K, into the dispersion medium, no thermal effect is observed. This observation allows us to assume that no chemical interaction takes place between cadmium telluride and water, methanol and ethanol.

The results obtained suggest the feasibility of using low-molecular alcohols such as methanol and ethanol as dispersion medium for modification of the surface of CdTe MCs by stabilizing molecules like TGA. These solvents are wetting well enough the surface of the CdTe MCs, as can be seen from the values of $\Theta \cos = 0.976$ and 0.980 (methanol) and $\Theta \cos = 0.991$ and 0.987 (ethanol) for oxidized and etched CdTe surface, accordingly. Such a good wettability ensures a good contact of the stabilizer molecules with the surface of CdTe MCs.

Moreover, due to low boiling point and low viscosity of the above low-molecular alcohols, they can be easily removed, if necessary, from the system by washing with deionized water. With that, optimum conditions for contact of TGA molecules with the CdTe surface are provided. This leads to the fact that at the adsorption of TGA from methyl and ethyl alcohol the formation of a saturated adsorption layer on the surface of the MK CdTe occurs at lower concentrations — 0.8 and 0.6 kg/m^3 , respectively (Fig. 1). However, relatively small geometric dimensions of molecules of methyl and ethyl alcohols, their high mobility and low work of adhesion practically do not allow them to compete with the TGA molecules in the formation of adsorption layer on the surface of cadmium telluride.

Upon achieving the dynamic equilibrium in the system, an exchange between adsorbed TGA molecules and free TGA molecule in solution takes place. The value of limit adsorption of TGA in the water being significantly lower (0.0016 g/d) compared to methyl (0.0030) and ethyl alcohol (0.0020 g/d) can be explained by poor wettability of MC surface with water (Fig. 1).

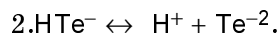
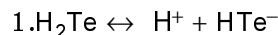
Colloidal CdTe NCs.

In [40] the possibility of synthesizing of colloidal CdTe NCs in anhydrous methanol using Na_2Te as the source of Te^{2-} ions was shown. However, it was impossible to synthesize CdTe NC in pure methanol or other monoatomic alcohols (i.e. without adding water) according to the protocol developed by us, because H_2Te (the source of Te^{2-}

ions, which is used in our protocol) is insoluble in methanol.

During the synthesis of colloidal CdTe NCs, their formation begins when the product of ion concentration $[\text{Cd}^{2+}][\text{Te}^{2-}]$ exceeds the solubility product (SP_{CdTe}). Accordingly, for the reaction to take place, the concentration of telluride ions must be high enough in order to exceed SP_{CdTe} .

Hydrogen telluride is dissolved in the water forming a weak acid that dissociates step-wise:



The first dissociation constant is $K_{\text{H}_2\text{Te}} = 2 \cdot 10^{-3}$.

Despite the ability of monoatomic alcohols to form hydrogen bonds, their molecular structure differs significantly from that of water. While in water a three-dimensional H-connections prevail, linear and cyclic associates predominantly formed in alcohols. The energy of hydrogen bonds in alcohols is factor of 1.4 higher than in water: 18.8 and 25.9 kJ/mol , respectively. Therefore, all gases like H_2E ($\text{E} = \text{S}, \text{Te}, \text{Se}$) dissociate very badly in monoatomic alcohols and their aqueous solutions. The rate of dissociation increases with alcohol concentration decline and reaches its maximum in clean water [16]. As a result, during the colloidal synthesis using as an anhydrous monoatomic alcohols as dispersion medium, hydrogen telluride passes through the reaction medium without reacting with cadmium ions and is almost completely exhausted and subsequently neutralized by 0.1 M sodium hydroxide, forming a fine black precipitate of Te.

For the above reasons, our study of influence of nature of the dispersion medium on properties of colloidal solutions was performed in conditions of synthesizing CdTe-TGA NCs in aqueous solutions of methanol and ethanol with a concentration of $5, 10, 25 \%$.

The PL spectra of CdTe-TGA NCs are presented in Fig. 3. The broad asymmetric shape of the PL bands indicates superposition of at least two channels of radiative recombination. In accordance with numerous previous works on CdTe and other II–VI compounds, they can be attributed to inter-band (excitonic) recombination and recombination through surface or other defect states [33, 41–43]. This composite structure of the PL band is most pronounced for CdTe-TGA NCs in pure water (Fig. 3a). In this spectrum the distinct maximum at

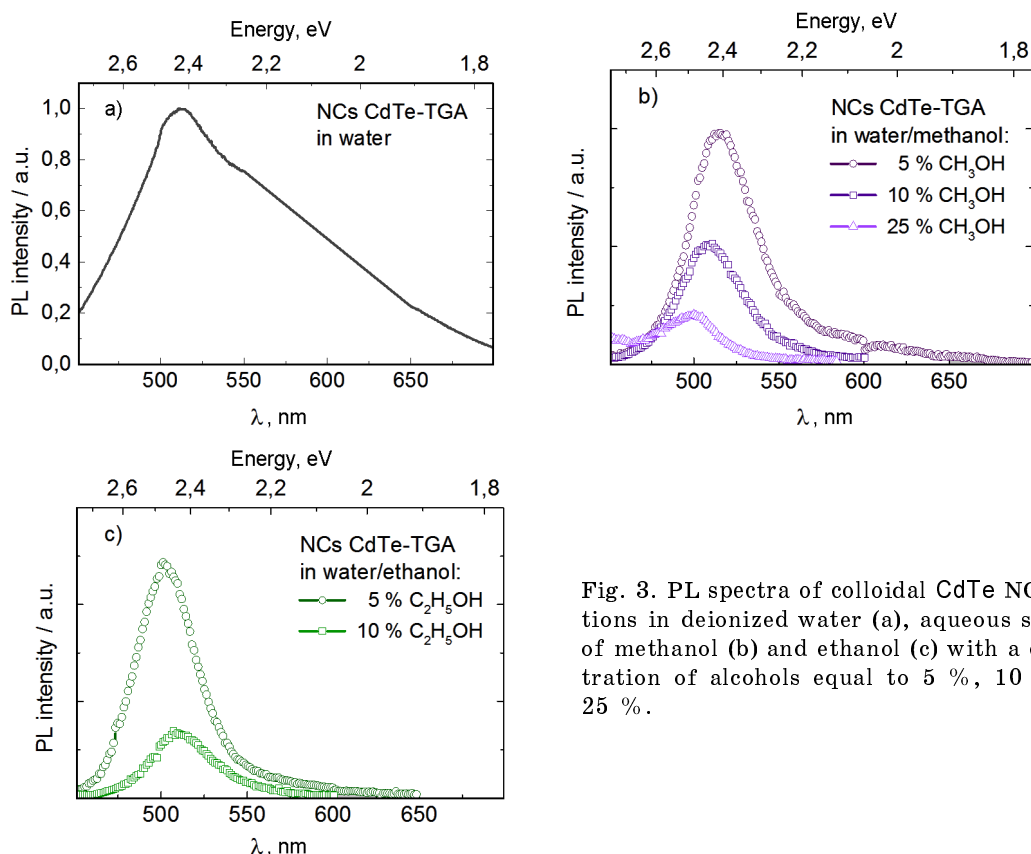


Fig. 3. PL spectra of colloidal CdTe NCs solutions in deionized water (a), aqueous solution of methanol (b) and ethanol (c) with a concentration of alcohols equal to 5 %, 10 % and 25 %.

about 520 nm (2.4 eV) can be attributed to the maximum of the excitonic band, while the overlapping broader contribution extending up to 700 nm is caused by defect and surface states [33]. Additional contribution to PL spectra comes from the ubiquitous size distribution in the NC sample.

The main common feature of all the spectra of aqueous NC solutions in mixture with alcohols is the absence of strong contribution of the defect related PL emission (Fig. 3 b,c). Contrary to NCs in pure water, the PL spectra of the latter reveal a dominated by the relatively narrow near-bandgap (excitonic) emission. This fact indicates what a tremendous role the solvent plays in the structure of the NC surface being related with their electronic states and optical properties. Very close spectral position of the excitonic feature in the water sample and in those with minimal (5 %) alcohol concentration further confirms that the effect of alcohol do not consist in changing the size or internal structure of the NCs, but predominantly affecting their surface properties. At higher alcohol concentration, however, a blue shift of the excitonic band is observed for methanol containing solutions and a red one for those with ethanol. This result indicates

that even minor difference in the nature of the alcohols can lead to opposite effects in the NC formation, thus leading to smaller and larger average NC size in the ensemble. The total PL intensity of the NCs in alcohol-containing solutions is, however, lower than in pure water, and it correlates well with concentration of particular alcohol (Fig. 3 b,c).

Analysis of the PL results obtained leads us to a conclusion that the two competing processes take place in the colloidal system under study. On one hand, the increasing concentrations of methanol leads to better wetting of the NC surfaces, thus facilitating the contact between the NCs and stabilizer molecules. On the other hand, the increasing concentration of methanol, as shown in [44], decreases the degree of H_2Te dissociation. As the concentration of Cd^{2+} ions is set constant, this leads to an increase $[\text{Cd}^{2+}]:[\text{Te}^{2-}]$ ratio in the reaction medium, resulting in smaller average size of NCs formed [45].

Using ethanol as a component of the dispersion medium causes non-monotonous changes in the PL spectra. At a concentration of 5 % the PL band maximum shift slightly to shorter wavelengths, while at

10 % ethanol PL larger shift to an opposite direction is observed (Fig. 3c). The trend towards decreasing of the PL intensity with ethanol concentration is qualitatively the same as in case of methanol-containing solutions.

Fig. 4 shows the PL decay curves of the colloidal CdTe NCs investigated in this study, registered at the maxima of corresponding PL band. The PL decay of an ensemble of identical fluorophores, which uniformly interact with environment and do not participate in the excited-state reaction, should be strictly single-exponential in a semi logarithmic scale [46]. It can be seen from the Fig. 4, however, that the decay curves of our CdTe NCs are not single-exponential, but can be satisfactorily fitted with two exponents. It should be noted, although, that non-exponential PL decay is a very common observation for colloidal semiconductor NCs of various compounds, both aqueous [47] and synthesized in high-boiling media [48], for both excitonic [49] and defect/surface-related emission [41, 50]. An unusual observation in our case is the absence of distinct dependence of the PL lifetime on the detection wavelength. This is in contrary to most of previous works on time-resolved PL of colloidal semiconductor NCs, which observe the wavelength-dependent decay, both for sharp excitonic emission [51] and broad-band defect- or surface-related emission [41]. In view of the absence of the of the wavelength dependence of the PL lifetime the two exponential components can be attributed to the non-radiative trapping of the photo-excited charge carriers to the (surface) defect states (fast component) and radiative recombination (slow component). Such interpretation is based in the literature on the additional data of PL decay measured at different PL wavelengths [49].

The bi-exponential character of the PL decay curves allows us to conclude that this is due to the static energy transfer in the investigated system, i.e. due to a direct contact of donor and acceptor. This phenomenon is generally explained by the Forster resonance energy transfer (FRET) model [52]. It resides on spectral overlap of the emission bands of donor and absorption band of acceptor, thus in case of NC ensemble with a finite size distribution providing a gradual energy transfer from smaller to larger NCs at the distances between NCs less than 10 nm.

It should be noted, however, that the CdTe NCs in colloidal solution are covered with a solvation shell that partially hinders

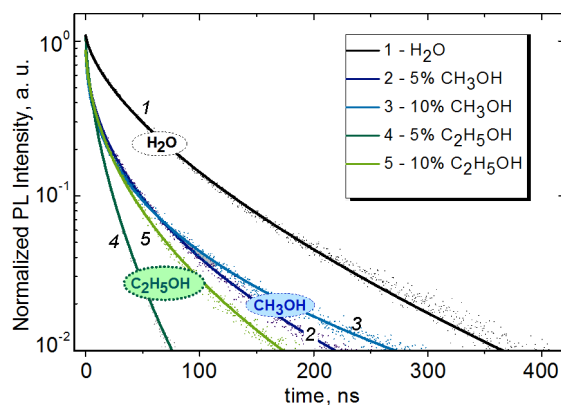


Fig. 4. PL decay of the colloidal CdTe NCs investigated in this work.

the interaction between NCs. Moreover, due to the negative (sign of the) surface charge, reduction of the dipole moment of the molecules of dispersion medium in the row "water > methanol > ethanol" leads to the decrease of the intensity of dispersion interaction between CdTe NCs and solvent molecules. Correspondingly, in the latter row the decreasing distance between the NCs will lead to stronger energy transfer and thus faster PL decay (Fig. 4).

4. Conclusions

It has been shown that introduction of finely grinded CdTe NCs into inorganic (water) and organic (methanol, ethanol) solvent results in their different surface properties, reflected in a different adsorption intensity of TGA molecules. This is supposed to be determined by the nature of the interaction between adsorbate (stabilizer) and adsorbent (CdTe) and by adhesive energy in the system solvent-CdTe. It has been found that the adsorption isotherms of CdTe NCs in water, methanol and ethanol are S-shaped. The intensity of adsorption of the stabilizing (TGA) molecules was found to be proportional to the wettability of the CdTe surface in the corresponding solvent. The nature of the dispersion medium was found to influence drastically at optical properties synthesized in this media by a colloidal (bottom-up) approach. In particular, adding monoatomic alcohols to the aqueous reacting solution increases the stability of the resulting colloid to sedimentation and eliminates the defect-related PL emission. However, the intensity of the excitonic emission in the alcohol-containing samples is partially reduced compared to purely water solutions.

In summary, the micro- and nanocrystalline CdTe obtained in this work are supposed to find applications in light-emitting devices and catalysis.

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